



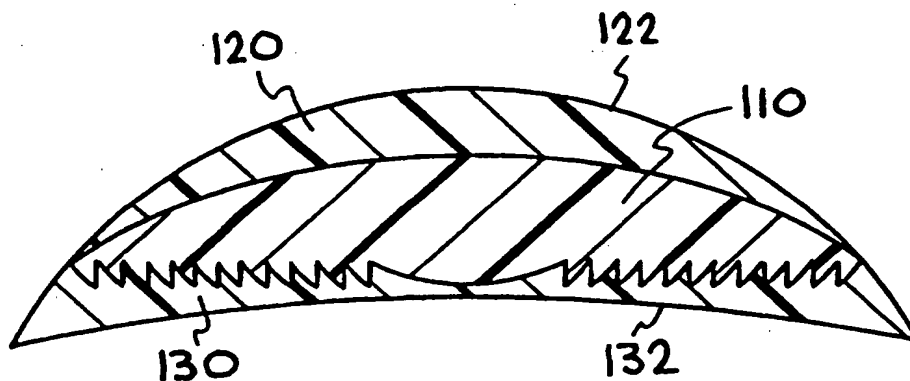
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US96/14535  <b>(22) International Filing Date:</b> 10 September 1996 (10.09.96)  <b>(30) Priority Data:</b> 08/530,395 14 September 1995 (14.09.95) US  <b>(71) Applicant:</b> THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 22nd floor, 300 Lakeside Drive, Oakland, CA 94612 (US).  <b>(72) Inventor:</b> TOEPPEN, John, S.; 5123 Felicia, Livermore, CA 94550 (US).  <b>(74) Agent:</b> SARTORIO, Henry, P.; P.O. Box 808, L-703, Livermore, CA 94550 (US).		<b>(81) Designated States:</b> CA, JP, KR, MX, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** STRUCTURED INDEX OPTICS AND OPHTHALMIC LENSES FOR VISION CORRECTION

**(57) Abstract**

An improved ophthalmic lens structure is described with macroscopically smooth exterior surface (122, 132) and internal optical structures (110) created within the volume of the lens (as shown in the figure). The material of which the lens is composed is optimally polymeric, nanoporous, and serves as a resin binder system to hold nanoparticles of mineral fillers having relatively high refractive indices in relative positions to lower refractive index materials to produce optical power by the control of light through refractive and diffractive structures (110). These structures can be generated using various combinations of machining, molding replication, optical exposure, and optical pattern generation techniques. These structures can be in the form of multiple laminated surface reliefs and/or volume holographic structures having radial, cylindrical, or asymmetric geometries.



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STRUCTURED INDEX OPTICS AND  
OPHTHALMIC LENSES FOR VISION CORRECTION

The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-48 between the United States Department of Energy and the University of California for the operation of Lawrence Livermore National Laboratory.

BACKGROUND OF THE INVENTION

This invention relates to improvements in an ophthalmic lens structure and the materials used in the formation of such lenses for vision correction. In particular, the invention relates to improvements in the structure and materials used in the formation of ophthalmic lens structures for vision correction.

In the design of corrective lenses to be worn in direct contact with the eye, as opposed to eyeglasses, certain design features must be compromised to accommodate the health and comfort of the user. Thus, while certain optical glasses are normally used as lens materials due to their high index of refraction, such hard and impervious materials are not entirely suitable for use in direct contact with the eye. Instead, soft plastic materials are used, such as hydrogels formed from acrylics which are sufficiently pliable to conform to the geometry of the eye so that the wearer does not experience discomfort, and which possess sufficiently porosity to pass tears, while blocking protein.

However, since such porous plastic materials do not have the high indices of refraction which many fully dense optical glasses possess, their use is somewhat limited in magnification or correction ability, since merely increasing the thickness of the lens will not suffice because such thick contact lenses are easily displaced, for example, when one blinks.

Thus, persons requiring a large amount of correction (wearers of "thick" glasses) cannot always be fitted with contact lenses.

In the past, the need for increased magnification for large and powerful glass lenses, such as used in the beacons of lighthouses, without undue increases in weight, resulted in the development of "Fresnel" lenses, i.e., a lens that has a surface consisting of a concentric series of simple lens sections so that a thin lens with a short focal length and large diameter is possible. Attempts have been made to import this Fresnel-type lens technology into the manufacture of ophthalmic lenses such as contact lenses, in particular to provide multifocal lenses to accommodate users needing both close vision and far vision correction, i.e., wearers of "bifocals". Futhey et al. U.S. Patent Nos. 4,830,481 and 5,229,797; and Simpson et al. U.S. Patent Nos. 5,076,684 and 5,116,111 all describe multifocal diffractive ophthalmic lenses which provide Fresnel-type lens geometries on one surface of the lens.

However, while the lens configurations described in the above patents can provide an increase in magnification of the resulting lens over prior art configurations, the resulting irregular surface of the Fresnel-type lens, if placed against the eye, would cause discomfort to the wearer. Furthermore the presence of such an irregular (non-smooth) surface, located on either the inner or outer surface of an ophthalmic lens, could present hygienic problems since such a rough surface would be difficult to satisfactorily clean. In addition, while the above-mentioned patents do not identify the types of materials used to construct such lenses, presumably the same types of low index of refraction plastic materials are used as are commonly used in the prior art to achieve the desired wearer comfort and biological compatibility with the eye.

Thus, there remains a need for an improved ophthalmic lens structure of high magnification formed from a material possessing a high index of refraction, preferably in combination with a material of low refractive index, while still providing comfort to the wearer and sufficient porosity to permit passage of tears and air therethrough.

### SUMMARY OF THE INVENTION

In accordance with the invention, an improved ophthalmic lens structure is provided comprising a first, preferably porous, non-toxic water-insoluble transparent plastic material filled with particles of non-toxic water-insoluble transparent inorganic filler having a refractive index higher than the transparent plastic material; an ophthalmic lens shape, such as a Fresnel-type lens, preferably formed in one surface of the first filled plastic material. The lens structure further includes a second, preferably porous, but unfilled, plastic material formed over the surface of the first transparent plastic material when an ophthalmic lens shape is formed in the surface. The ophthalmic lens structure may also comprise a plurality of lenses, formed by alternating high refractive index filled (or unfilled) plastic material and low refractive index unfilled plastic materials in a stack to provide adjoining materials respectively of high and lower refractive indices, with smooth surfaces, however, provided on both outer surfaces of the stack.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a top view of a harmonic Fresnel-type lens shape which may be used in forming the ophthalmic lens of the invention.

Figure 2 is a vertical side-section view of the Fresnel-type lens shape of Figure 1.

Figure 3 is vertical cross-sectional view of a mold used to form the high Refractive Index portion of the ophthalmic lens of the invention.

Figure 4 is a vertical cross-sectional view of the high Refractive Index portion of the ophthalmic lens structure of the invention formed in Figure 3.

Figure 5 is a vertical cross-sectional view of another mold used in another embodiment of the invention.

Figure 6 is a vertical cross-sectional view of the final form of one embodiment of the ophthalmic lens structure of the invention.

Figure 7 is a vertical cross-sectional view of another embodiment of the ophthalmic lens structure of the invention.

Figure 8 is a vertical cross-sectional view of still another embodiment of the ophthalmic lens structure of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

~~The invention, in its simplest form, comprises an improved~~ ophthalmic lens structure comprising a first, preferably porous, transparent plastic material filled with inorganic filler material having a refractive index of at least about 1.7 and a particle size not exceeding about 50 nanometers. In a preferred embodiment, an ophthalmic lens shape, such as a Fresnel-type lens, is formed in at least one surface of the filled plastic material; and a second, also preferably porous, but unfilled transparent plastic material is formed over the surface of the first plastic material having the ophthalmic lens shape formed therein.

By use of the term "ophthalmic lens structure" herein is meant a vision correction lens structure intended for use in direct contact with the human eye, such as a contact lens, or as an implanted intraocular lens (IOL). By use of the term "microprismatic" is meant a surface comprising a plurality of tiny prisms. By use of the term "Fresnel-type lens" herein is meant a lens that has a surface consisting of a concentric series of simple lens sections thereby forming a thin lens with a short focal length and large diameter, compared to a single lens of the same focal length.

A modified fresnel lens may also be formed by modulating the refractive index of a material rather than its surface. Such a lens would consist of a series of periodic features where the optical thickness or thinness of the material could correspond to the hills and valleys of a normal fresnel. This is accomplished either by controlling the relative porosity or the percentage of mineral loading in these areas. This is, in effect, a gradient index fresnel lens.

##### a. Transparent Plastic Lens Material

The transparent plastic lens material used in the practice of the invention is formed from a biologically compatible (non-toxic) water-insoluble transparent polymerizable plastic material. Examples of such biologically compatible water-insoluble transparent polymerizable plastic material, (or polymeric plastic materials, the monomers of which may be

used to form the ophthalmic plastic lens structure of the invention) include acrylates (e.g., capable of polymerizing to form poly(methyl)methacrylate), styrene, carbonate (e.g., capable of polymerizing to form polycarbonate), allyl diglycol carbonate, poly(styrene-acrylonitrile) copolymer, poly(styrene-methacrylate) copolymer, poly(4-methyl-1-pentene), silicones, polyvinyl carbazole, polyvinyl alcohol, polyvinyl cinnamate, polyphenols, polytetrafluoroethylene, and epoxies, and may also include esters, and urethanes.

**b. Porosity of Transparent Plastic Lens Material**

The transparent plastic lens material just described preferably capable of being formed with a porosity sufficient to permit the passage of a saline solution (such as tears) to pass therethrough, but with pores insufficiently large to permit the passage of protein therethrough. Usually the pores to be formed in the polymerized plastic material will range in size from about 5 nanometers (nm) to about 300 nm.

Such porosity may be formed and controlled in the polymerized plastic material by any one of a number of means, including chemical means such as by forming a colloid of the polymerizable plastic lens material with another extractable material (solid or liquid) suspended in the resulting polymerized matrix, and then removing the extractable suspended material by a suitable solvent. The desired porosity could also be formed using photolithographic techniques by exposing photopolymerizable monomers to fine patterns of light such as generated by interferometry and holographic techniques, followed by removal of the remaining unexposed and therefore unpolymerized monomeric portions with suitable solvents, e.g., the exposure of acrylic monomers to suitable light patterns to polymerize the exposed portions, followed by washing with alcohol to remove unexposed acrylic monomers, leaving a porous acrylic polymer. These techniques for controlling the porosity of the plastic lens material may also be utilized to use the porosity of the polymer to create optical power by a technique similar to volume holography.

**c. High Refractive Index Transparent Inorganic Filler**

The filler material to be used in conjunction with the above described transparent polymeric plastic material must comprise a material

having a refractive index of at least 1.7, in accordance with the invention, to impart to the filled plastic material the desired increase in refractive index. This will usually require the use of a biologically compatible (non-toxic) water-insoluble transparent inorganic filler material. Furthermore, the maximum particle size of the filler material must be controlled to be smaller than about 1/10 of the wavelength of visible light to preserve the transparent appearance of the lens, i.e., small enough that the particles of filler material will not scatter visible light. Since visible violet light has a wavelength of about 410 nm or 4100 Angstroms, the particle size should not exceed about 40 nm, and preferably should not exceed about 25 nm. Preferably, the geometry of the filler material will be spherical, but other geometric shapes may be used and should be deemed to be within the scope of the invention. Materials of this kind are usually made by sol-gel techniques utilizing hydrolysis and condensation as is well known to those skilled in the art.

The maximum amount of such high refractive index particulate filler material used in the transparent polymeric plastic material may vary with the particular polymerized material. In accordance with the invention, however, the minimum amount of such filler material will be at least about 20 volume % of the combined total of monomer and filler material initially blended together, and typically the amount of loading will range from about 20 volume % to about 85 volume %.

Examples of high refractive index inorganic filler materials suitable for use in the practice of the invention include diamond (R.I. 2.4580), strontium titanate (R.I. 2.6320), titanium dioxide (brookite) (R.I. 2.2583, 2.586, 2.741), titanium dioxide (octahedrite, anatase) (R.I. 2.554, 2.493), titanium dioxide (rutile) (R.I. 2.616, 2.903), barium monosulfide (R.I. 2.155), cadmium oxide (R.I. 2.49), chromium oxide ( $\text{Cr}_2\text{O}_3$ ) (R.I. 2.5), magnesium sulfide (R.I. 2.271), strontium monosulfide (R.I. 2.107), tin oxide (R.I. 2.106), zirconium oxide, and aluminum oxide. Other metal salts and oxides may be used, e.g., other oxides, sulfides, nitrides, and fluorides, provided that they are transparent, non-toxic, water-insoluble, and have a refractive index of at least about 1.7.



#### d. Formation of Lens Surface

When an ophthalmic lens surface is formed in the ophthalmic lens structure of the invention, such a shape may be formed either by molding the lens, using a master mold in which the shape of the desired lens is formed, or by using holographic and photolithographic techniques, or some combination thereof.

When using the first technique, particularly when a multiple surface or faceted lens such as a Fresnel-type lens is to be formed, a cylindrical master mold piece, such as a metal mold piece, is engraved to form the desired shape of the Fresnel-type lens therein. Referring to Figures 1 and 2, by way of an example of the shape of a Fresnel-type lens, a master lens mold piece 2 is generally shown having a planar surface 4 in which is engraved a Fresnel-type lens structure which comprises a central spherical segment or dished out portion 10 (which could be either concave or convex) having a radius  $r_0$  to a focal point F. Surrounding spherical segment 10 are a series of concentric lens sections, shown as 20, 30, and 40 in Figures 1 and 2, and having respective radii,  $r_2$ ,  $r_3$ , and  $r_4$  which also intersect focal point F. The Fresnel-type lens may have a diminution of ring size (distance across the ring) from center to edge, as shown in Figures 1 and 2, or may have uniform ring widths, or uniform ring depths.

After formation of the master mold surface, the engraved mold surface is placed in a mold; a polymerizable monomer is poured into the mold, and a lens image is molded into the plastic material to be used for formation of the ophthalmic lens structure of the invention, as will be described in more detail below.

Alternatively, instead of forming a master mold, (or in addition to) the ophthalmic lens shape (such as a Fresnel-type shape) may be molded into the plastic lens material using holographic and photolithographic techniques. In this case, the plastic material to be used in the formation of the ophthalmic lens structure of the invention is selected to be a monomeric mixture capable of photo-polymerization, upon being exposed to a pattern of light, with the resulting polymer capable of then forming a relief image.

In this method, a holographic image of the desired lens pattern is imposed on the monomer, and the unpolymerized portions of the plastic material is washed away with a suitable solvent. Such a method of ~~holographically forming patterns in photopolymerizable plastic materials is~~ described, for example, by James J. Cowman in "The Recording and Large Scale Replication of Crossed Holographic Grating Arrays using Multiple Beam Interferometry", published in SPIE Vol. 503 Applicant, Theory, and Fabrication of Periodic Structures (1984) at pp 120-129, the subject matter of which is hereby incorporated by reference.

In accordance with the invention, the plastic material, after exposure to the light pattern and polymerization, is then soaked in a liquid which will extract the unpolymerized material, leaving the polymerized material in place causing density differences corresponding to the holographic image photopolymerized in the plastic material. This, in turn, results in the lens pattern being reproduced as a multiple density pattern in the polymerized structure, i.e., a structure having the same optical effect on a beam of light passing therethrough as would a lens pattern cut or molded into the surface of the plastic material as with the earlier discussed method of forming the lens structure.

e. Formation of Stack of High and Low Refractive Index Lens Layers

When the desired lens pattern, such as a Fresnel-type lens surface, has been engraved in a master mold piece, e.g., in a metal mold piece, the engraved mold piece is then loaded into a mold and the desired Fresnel lens shape is then cast from one of the previously discussed plastic materials. Turning now to Figure 3, master mold piece 2, having the desired ophthalmic lens shape (e.g., a Fresnel lens pattern) engraved thereon, is mounted into one end of a mold 60, which preferably is cylindrical in cross section. Polymerizable plastic material 100, having the high refractive index filler material already loaded therein, is then poured into mold 60 over engraved face 4 of master mold piece 2. A second cylindrical mold piece 70, which may be provided with a convex or concave spherical surface, is then placed over polymerizable plastic material 100 and polymerizable plastic material 100 is allowed to at least partially cure,

depending upon the method to be employed to render the molded material porous.

When the porosity will be obtained by leaching out a second (non-polymerizable) material which is dispersed, for example as a separate phase, in polymerizable material 100, polymerizable material 100 may be completely cured, and then removed from the mold and treated to remove the second (non-polymerizable) material, thus leaving a porous matrix of the polymerized material with the desired ophthalmic shape molded into one surface thereof. Alternatively, polymerizable material 100 may be only partially cured, then subjected to the porosity treatment to remove the non-polymerizable material, and then subjected to either heat or light energy, e.g., baked at 120°F, to fully cure the polymerizable material, resulting in the structure shown at 110 in Figure 4:

When the porosity is to be obtained by photolithographic means, a blank or disc of the polymerizable material (e.g., polymerizable material 100) is partially cured in a mold, then optionally removed from the mold and subjected to a suitable pattern of light, to fully cure those portions of the polymerizable material exposed to the light pattern, followed by a solvent treatment to remove unpolymerized portions of the polymerizable material. The resulting porous polymerized plastic lens structure may then be cured by baking or by light energy, if required, as previously described above, resulting again in the final ophthalmic lens structure 110 of the invention depicted in Figure 4.

Alternatively, when the desired ophthalmic lens shape is to be formed using holographic and photolithography techniques, a blank mold piece 80, which may be provided with a concave or convex spherical head or surface 82 thereon, is mounted in cylindrical mold 60 and polymerizable material 100 is then loaded into mold 60 over surface 82, as shown in Figure 5. Prior to insertion of mold piece 70 into mold 60 in contact with the opposite surface of polymerizable material 100, material 100 is exposed to the previously described holographic and photolithographic steps to form the density lens image therein. Mold piece 70 is then placed in contact with the upper surface of the gel material and the material is allowed to partially polymerize. The partially cured gel may then be

removed from the mold, subjected to the previously described porosity process, and then, optionally, finally cured either by heat, e.g., at a temperature of 120°F, or by optical exposure.

In either event, after the formation of the ophthalmic lens shape, such as a Fresnel-type lens shape, in the porous polymerized plastic material filled with the high Refractive Index inorganic filler material, compound lenses or stacks of lenses and eye pieces can then be formed, as desired. For example, as shown in Figure 6, further layers of plastic material 120 and 130 may be bonded to molded ophthalmic lens structure 110. The plastic material used to form layers 120 and 130 may comprise the same polymerizable monomer, but layers 120 and 130 are not filled with the high Refractive Index filler material (to avoid destroying the lens effect when the ophthalmic lens shape, e.g., a Fresnel-type lens shape, is molded into material 100). This would have the added benefit of providing external surfaces to the lens stack which would not have the filler material embedded therein, since the techniques used to form the porosity in filled plastic material 100 will also uncover some of the filler material, which could result in an abrasive surface if the filler material was not spherically shaped. That is, the respective surfaces 122 and 132 of layers are smooth, making them easier to clean and, of course, the inner smooth surface 132 is more acceptable for direct contact with the human eye.

Figure 7 shows yet another embodiment wherein a multiple lens structures is formed. In the illustrated embodiment, a polymerizable material with a high Refractive Index filler material is again used for lens structure 140 wherein a first Fresnel-type lens surface 142 is molded on one surface of double Fresnel-type lens structure 140, and a second Fresnel-type lens surface 144 is molded into the opposite surface of Fresnel-type lens 140. As in the structure of Figure 6, low Refractive Index unfilled plastic materials are used to form layers 120\_ and 130\_ which are molded to opposite surfaces 142 and 144 of double Fresnel-type lens structure 140 resulting in the same type of smooth outer surfaces (122\_ and 132\_) of the lens stack as shown in the previous embodiment of Figure 6.

More than one layer of lenses can be used in the structure in the same manner, as shown in the embodiment of Figure 8, wherein two

double surfaced Fresnel-type lens structures, 150 and 160, are shown formed from polymerizable material with a high Refractive Index filler material, and separated from one another by a layer 170 formed from low Refractive Index material which is also used to form outer layers 180 and 190.

While specific embodiments of the ophthalmic lens structure of the invention have been illustrated, and specific methods of forming the ophthalmic lens structure of the invention have been described, in accordance with this invention, modifications and changes of the apparatus, parameters, materials, etc. will become apparent to those skilled in the art, and it is intended to cover in the appended claims all such modifications and changes which come within the scope of the invention.

**WHAT IS CLAIMED IS:**

1. An improved ophthalmic lens structure comprising a first non-toxic water-insoluble transparent plastic material filled with homogeneously dispersed particles of non-toxic water-insoluble transparent inorganic filler having a refractive index higher than the transparent plastic material.
2. The ophthalmic lens structure of claim 1 wherein said inorganic filler material has a refractive index of at least 1.7.
3. The ophthalmic lens structure of claim 2 wherein said particles of inorganic filler material have a particle size not exceeding about 40 nanometers.
4. The ophthalmic lens structure of claim 2 wherein said particles of inorganic filler material are spherical shaped.
5. The ophthalmic lens structure of claim 2 wherein said first filled plastic material is porous.
6. The ophthalmic lens structure of claim 5 wherein the pore size of said porous said first filled plastic material ranges from about 5 nm to about 300 nm.
7. The ophthalmic lens structure of claim 2 wherein said particles of inorganic filler material comprises at least about 20 volume % of the total volume of said first filled plastic material and said inorganic filler material therein.
8. The ophthalmic lens structure of claim 2 wherein said particles of inorganic filler material comprises from about 20 volume % to about 80 volume % of the total volume of said first filled plastic material and said inorganic filler material therein.

9. The ophthalmic lens structure of claim 2 wherein an ophthalmic lens shape is formed in one surface of said first filled plastic material.

10. The ophthalmic lens structure of claim 9 which further comprises a second porous but unfilled non-toxic, water-insoluble, transparent plastic material formed over said one surface of said first porous plastic material having said ophthalmic lens shape formed therein.

11. An improved ophthalmic lens structure comprising:

a) a first porous, non-toxic, water-insoluble, transparent plastic material filled with at least about 20 volume % of a non-toxic, water-insoluble, transparent inorganic filler material homogeneously dispersed therein and having a refractive index of at least 1.7 and a particle size not exceeding about 40 nanometers;

b) an ophthalmic lens shape formed in one surface of said first porous filled plastic material; and

c) a second porous but unfilled porous, non-toxic, water-insoluble, transparent plastic material formed over the surface of said first porous plastic material having said ophthalmic lens shape formed therein.

12. The ophthalmic lens structure of claim 11 wherein said inorganic filler material is selected from the group consisting of a metal oxide, a metal sulfide, a metal nitride, a metal fluoride, and mixtures thereof.

13. The ophthalmic lens structure of claim 11 wherein said inorganic filler material is selected from the group consisting of diamond, strontium titanate, titanium dioxide, titanium dioxide, titanium dioxide, barium monosulfide, cadmium oxide, chromium oxide ( $\text{Cr}_2\text{O}_3$ ), magnesium sulfide, strontium monosulfide, tin oxide, zirconium oxide, and aluminum oxide.

14. The ophthalmic lens structure of claim 11 wherein said inorganic filler material comprises spherical particles homogeneously dispersed in said first porous plastic material.

15. The ophthalmic lens structure of claim 1 wherein said porous plastic material has a pore size ranging from about 5 nm to about 300 nm.

16. The ophthalmic lens structure of claim 11 wherein said porous plastic material comprises a material selected from the group consisting of acrylates, styrene, carbonates, styrene-acrylonitrile copolymers, ~~styrene-methacrylate copolymers, poly(4-methyl-1-pentene),~~ silicones, epoxies, esters, polyvinyl carbizol, polyvinyl alcohol, polyvinyl cinnemate, polyphenols, and urethanes.

17. The ophthalmic lens structure of claim 11 wherein said ophthalmic lens shape formed in one surface of said first porous filled plastic material comprises a Fresnel-type lens shape.

18. The ophthalmic lens structure of claim 11 wherein said second porous plastic material has a second ophthalmic lens shape formed on an opposite surface thereof from the surface of said second material facing said first ophthalmic lens shape formed in said first material; and said structure further comprises a third porous plastic material formed over said surface of said second material having said second ophthalmic lens shape formed therein, said third porous plastic material comprising a plastic material also filled with inorganic filler material having a refractive index of at least 1.7 and a particle size not exceeding about 40 nanometers.

19. The ophthalmic lens structure of claim 11 wherein said second porous plastic material has a second ophthalmic lens shape formed on an opposite surface thereof from the surface of said second material facing said first ophthalmic lens shape formed in said first material; and said structure further comprises a third porous non-toxic, water-insoluble, transparent plastic material formed over said surface of said second material having said second ophthalmic lens shape formed therein, said third porous plastic material comprising a plastic material also filled with inorganic filler material having a refractive index of at least 1.7 and a particle size not exceeding about 40 nanometers.

20. The ophthalmic lens structure of claim 11 wherein said first porous plastic material has a second lens shape formed on an opposite surface thereof from the surface of said first porous plastic material having said first ophthalmic lens shape formed therein; and said structure further comprises a third porous, non-toxic, water-insoluble, transparent plastic material formed over said second lens shape formed in said first porous



plastic material, said third porous plastic material also comprising an unfilled porous plastic material.

21. The ophthalmic lens structure of claim 11 wherein said first porous plastic material has a second ophthalmic lens shape formed on an opposite surface thereof from the surface of said first porous plastic material having said first ophthalmic lens shape formed therein; and said structure further comprises a third porous, non-toxic, water-insoluble, transparent plastic material formed over said second ophthalmic lens shape formed in said first porous plastic material, said third porous plastic material also comprising an unfilled porous plastic material.

22. An improved ophthalmic lens structure comprising:

- a) a first porous, non-toxic, water-insoluble, transparent plastic material filled with porous, non-toxic, water-insoluble, transparent inorganic filler material having a refractive index of at least 1.7 and a particle size not exceeding about 40 nanometers;
- b) an ophthalmic lens shape formed by a holographic image in said first porous filled plastic material; and
- c) a second porous but unfilled non-toxic, water-insoluble, transparent plastic material formed over at least one surface of said first porous plastic material having said ophthalmic lens shape formed therein.

23. The ophthalmic lens structure of claim 22 wherein said inorganic filler material comprises spherical particles dispersed in said first porous plastic material.

24. An improved ophthalmic lens structure comprising:

- a) a first porous, non-toxic, water-insoluble, transparent plastic material filled with spherically shaped non-toxic, water-insoluble, transparent, inorganic filler material having a refractive index of at least 1.7, a particle size not exceeding about 40 nanometers, and a pore size ranging from about 5 nm to about 300 nm;
- b) a Fresnel-type ophthalmic lens shape formed in one surface of said first porous filled plastic material; and
- c) a second porous but unfilled non-toxic, water-insoluble, transparent plastic material formed over the surface of said first porous

plastic material having said Fresnel-type ophthalmic lens shape formed therein.

25. An improved ophthalmic lens structure comprising:

- ~~a) a first porous, non-toxic, water-insoluble, transparent~~  
plastic material having a refractive index of at least 1.7;
- b) an ophthalmic lens shape formed in one surface of said first porous filled plastic material; and
- c) a second porous but unfilled porous, non-toxic, water-insoluble, transparent plastic material formed over the surface of said first porous plastic material having said ophthalmic lens shape formed therein.

26. An improved ophthalmic lens structure comprising a gradient index fresnel lens produced by the creation of periodic microgradients of controlled refractive indices within the volume of a single layer of filled or unfilled polymer material.

27. The improved ophthalmic lens structure of claim 26 in combination with another layer of material.

1 / 4

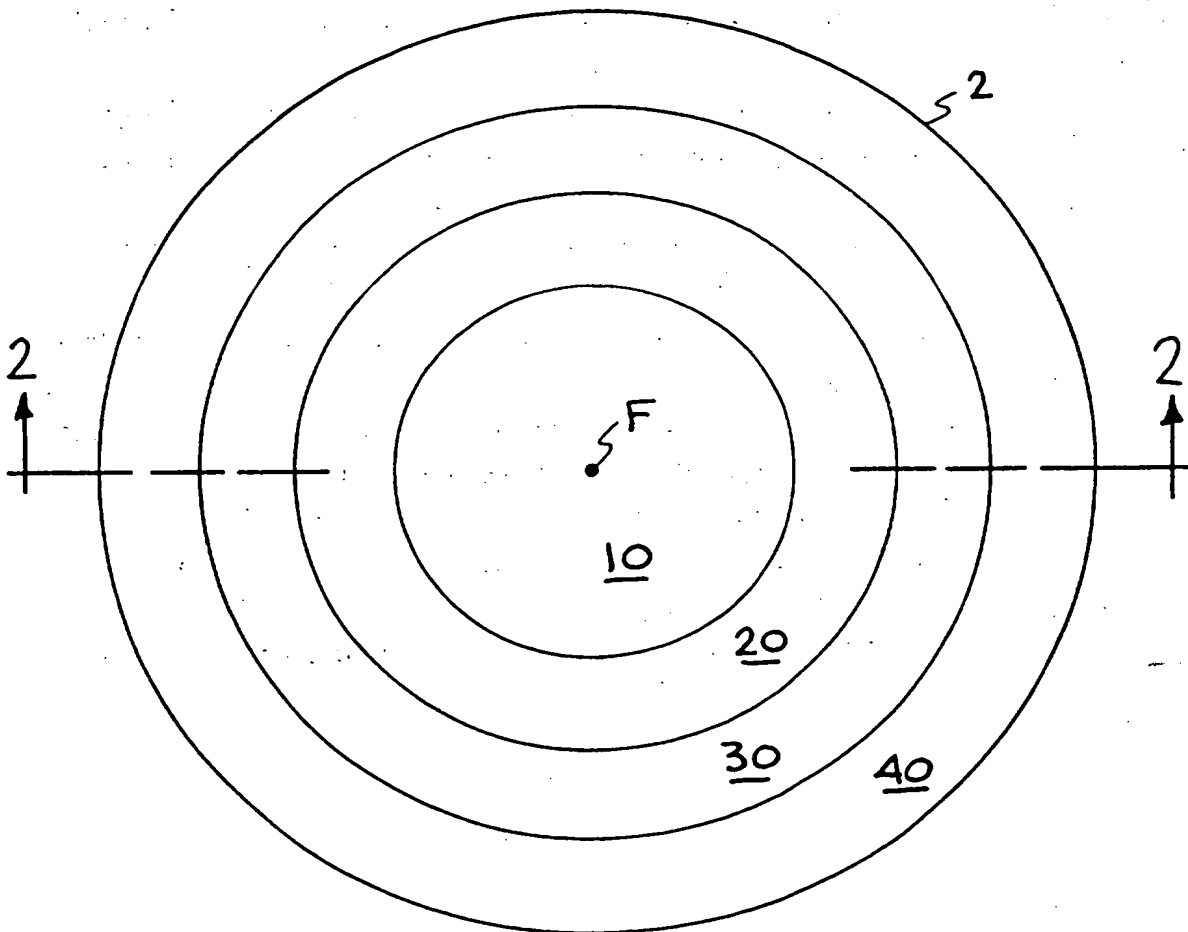


FIG. 1

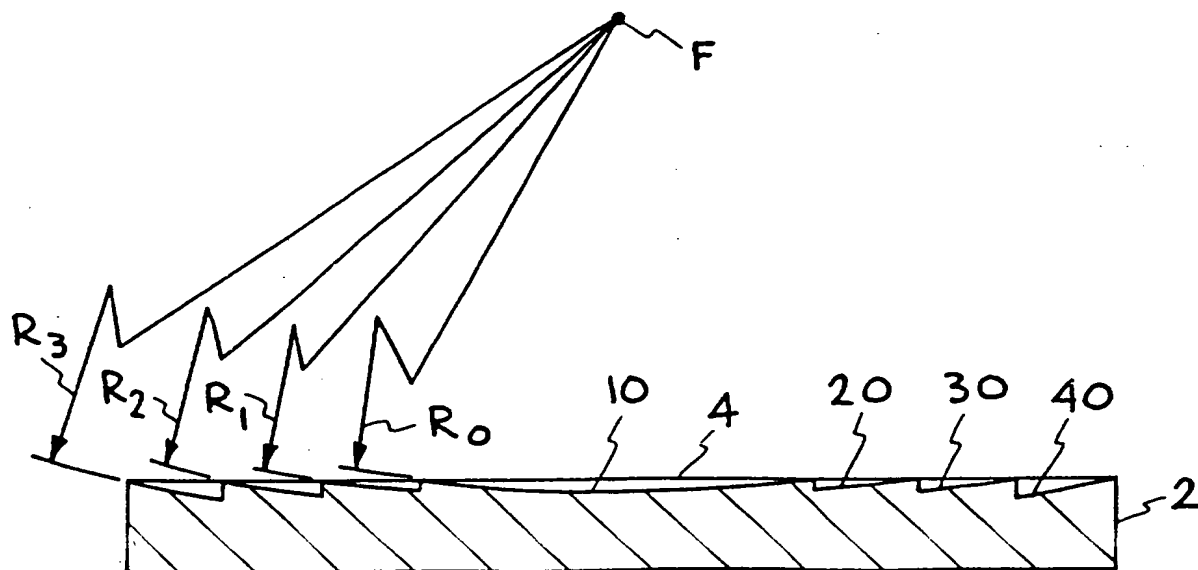


FIG. 2

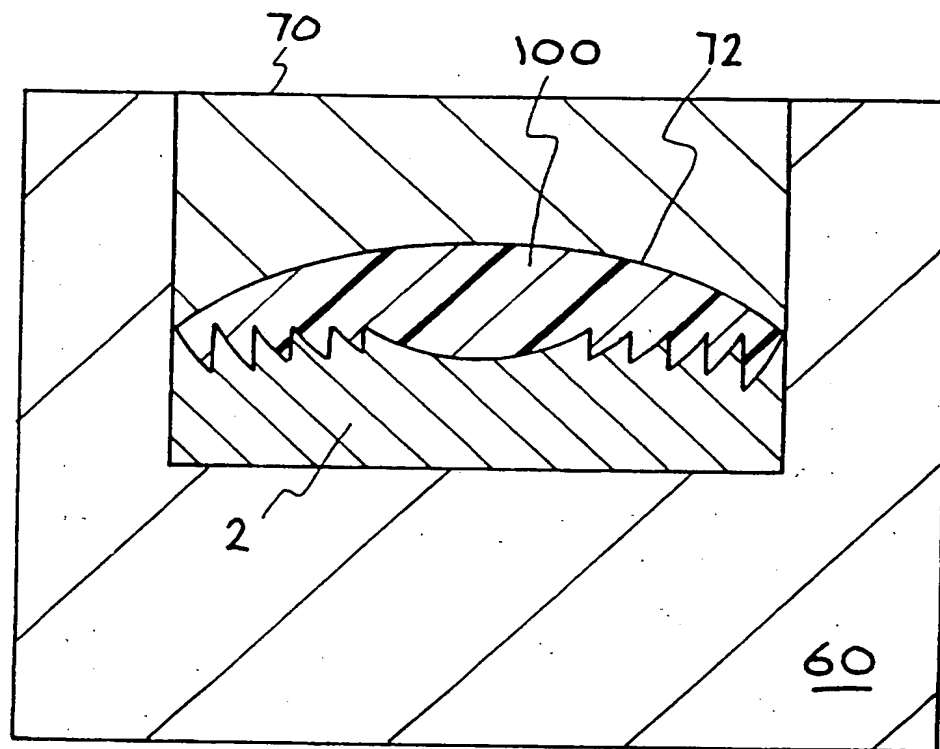


FIG. 3

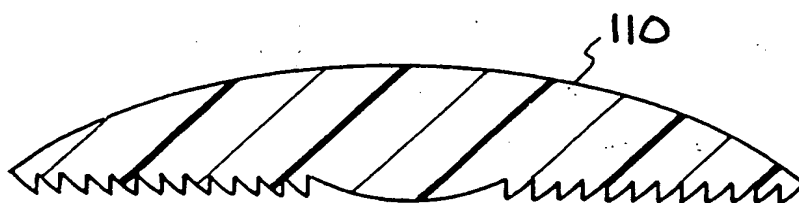


FIG. 4

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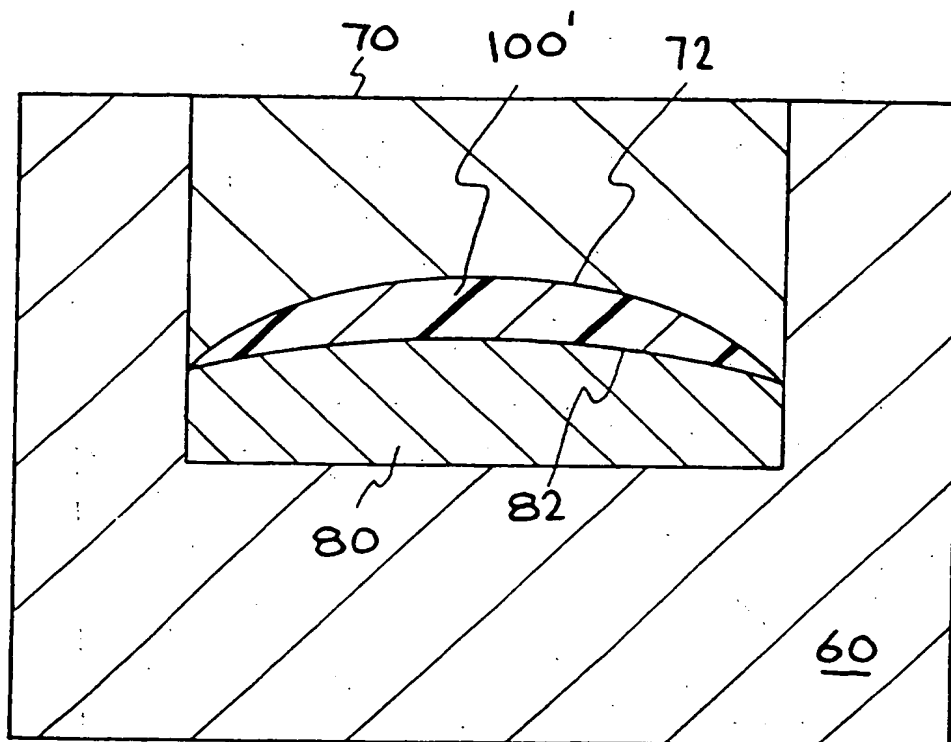


FIG. 5

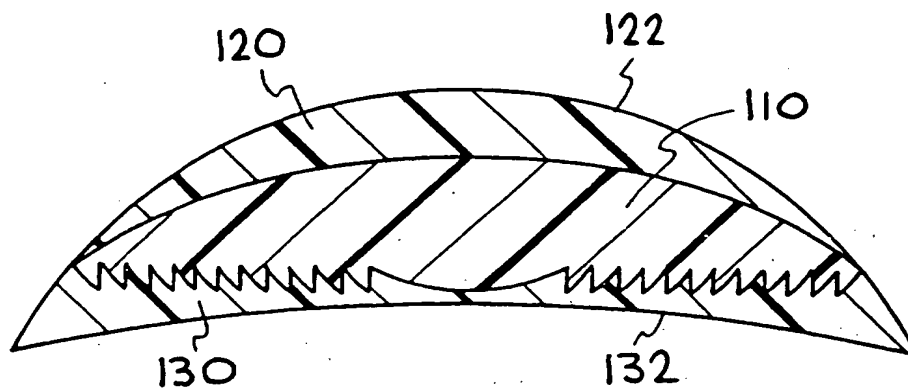


FIG. 6

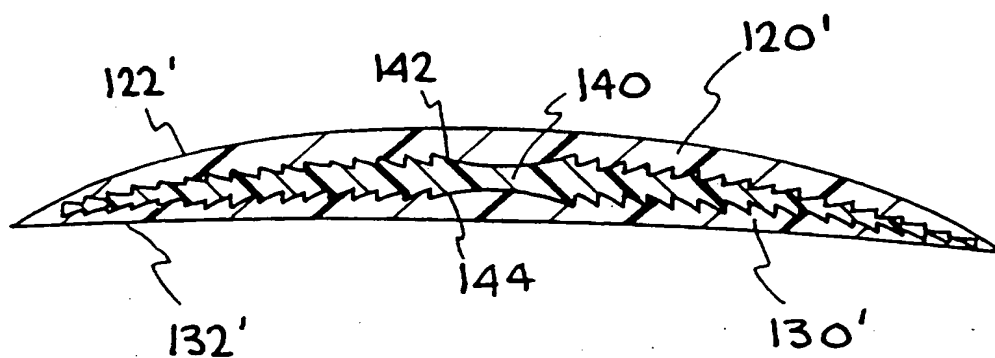


FIG. 7

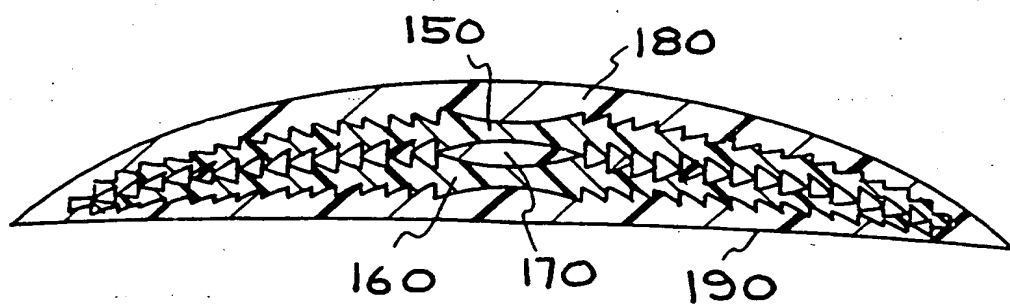


FIG. 8

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/14535

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/106; 264/1.32, 1.7; 427/2.24; 359/742; 623/6; 428/315.9, 317.9

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 3,557,261 A (WICHTERLE) 19 January 1971, abstract, column 2, line 50 to column 3, line 27, example 3 and claim 4.	1-2, 4-10 ----- 1-17, 22-26
X -- Y	US 5,160,463 A (EVANS et al.) 03 November 1992, column 1, line 64 to column 2, line 15, column 2, lines 55-68, column 3, lines 40-45, column 7, lines 26-33, and examples 1, 5, and 8.	1-2, 4-10 ----- 1-17, 22-26
X -- Y	EP 0,384,632 A (PILKINGTON VISIONCA) 29 August 1990, abstract, preferred and example.	1-2, 4-10 ----- 1-17, 22-26
Y	US 5,300,116 A (CHIRILA et al.) 05 April 1994, abstract and column 6, lines 14-46.	1-27

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
16 DECEMBER 1996

Date of mailing of the international search report

14 JAN 1997

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Authorized officer  
ANDREW E. C. MERRIAM

Facsimile No. (703) 305-3230

Telephone No. (703) 308-2351

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/14535

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,034,166 A (RAWLINGS et al.) 23 July 1991, abstract, <del>column 4, line 61 to column 5, line 15 and column 6, line 63 to</del> column 7, line 38.	1-27
Y	US 5,253,103 A (BOYD et al.) 12 October 1993, column 4, lines 53-60 and column 20, lines 55-57.	1-27
Y	US 4,746,691 A (FUHRMAN) 24 May 1988, column 3, lines 21-45.	1-27
Y	US 5,152,788 A (ISAACSON et al.) 06 October 1992, abstract, column 3, lines 29-60, column 4, lines 12-23 and column 9, lines 8-16.	1-27
Y	US 5,076,684 A (SIMPSON et al.) 31 December 1991, abstract, column 1, lines 1-24, column 2, lines 3-15 and 39-53 and column 3, lines 5-37.	1-27
Y	US 5,106,533 A (HENDRICKSON et al.) 21 April 1992, abstract, column 5, lines 15-56, column 9, lines 33-55 and column 13, lines 5-15.	1-27
Y	US 4,663,358 A (HYON et al.) 05 May 1987, abstract, column 1, lines 23-30, column 2, lines 22-30 and column 3, lines 18-54.	16
Y	REES and LEINER, eds., "Gradient-Index Optics and Miniature Optics", SPIE, Vol. 935, April, 1988, page 102.	22-26



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/14535

## A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

G02C 7/04; G02B 3/00, 3/08; C08K 3/04, 3/08, 3/22; B29D 11/00; B05D 3/00

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

523/106; 264/1.32, 1.7; 427/2.24; 359/742; 623/6; 428/315.9, 317.9

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